Electrohydrodynamic atomization of Balangu (*Lallemantia royleana*) seed gum for the fast-release of *Mentha longifolia* L. essential oil: characterization of nano-capsules and modeling the kinetics of release

Hassan Rezaeinia[1], Behrouz Ghorani[1], Bahareh Emadzadeh[1]& Nick Tucker[2]

1 Department of Food Nanotechnology, Research Institute of Food Science and Technology (RIFST), Km 12 Mashhad-Quchan Highway, Mashhad, Iran, P.O.Box : 91895-157-356

2 University of Lincoln, School of Engineering, Brayford Pool, Lincoln, LN6 7TS, United Kingdom (UK)

Abstract

The aim of this study is to optimize encapsulation of *Mentha longifolia* L. essential oil into Balangu (*Lallemantia royleana)* seed gum nano-capsules, to increase their utility as flavoring and bioactive agents in foods and beverages. Essential oil emulsions with Balangu seed gum (0.25 and 0.5% w/w) and various polyvinyl alcohol (PVA) concentrations (0.5, 1 and 2%) combined with Tween-20 (0.06, 0.08 and 0.1%) were electrosprayed. Increasing the concentration of PVA increased the emulsion viscosity and improved both loading capacity (77.56 to 84.68%) and encapsulation efficiency (81.54 to 87.82 %) of the essential oil within the structure of the Balangu gum nano-capsules. Field emission scanning electron microscopy (FESEM) indicated that by increasing the amount of the gum (from 0.25 to 0.5%) and PVA (from 1 to 2%), the process could be made to produce nanofibers. The *Mentha longifolia* L. essential oil was entrapped in nanostructures without any chemical interaction with encapsulant material, this was demonstrated by Fourier transform infrared spectroscopy and differential scanning calorimetry. The release mechanisms and kinetics of loaded *Mentha longifolia* L. essential oil were evaluated in different simulated food models (aqueous, acidic, alcoholic or alkalic and oily food models) and release profiles data were fitted to first order, Kopcha, Korsmeyer-Peppas, and Peppas-Sahlin models. The essential oil release profiles fitted well to the Peppas-Sahlin model for a range of simulated foods. The release mechanism of the essential oil from the nanostructure of the Balangu seed gum is mainly controlled by the Fickian diffusion phenomenon.

Keywords: Electrohydrodynamic atomization, Balangu seed gum, nano-capsule, *Mentha longifolia* L, kinetics of release, fast release.

1. Introduction

The term "nutraceutical" is a portmanteau of nutrition and pharmaceutical and refers to foods containing bioactive compounds found which in addition to the nutritional characteristics are claimed to improve human health by means of biochemical properties such as antioxidant activity and radical scavenging (Zlotogorski, et al., 2013b), with various effects being claimed such as anti-cancer properties (Zlotogorski, et al., 2013a), and improvement to oral diseases (McClements & Xiao, 2017). There are several compounds in both natural and processed foods for which nutraceutical properties are claimed including carotenoids, flavonoids, curcuminoids, phytosterols and certain fatty acids (Gupta, 2016).

Mentha longifolia L. is a medicinal and aromatic herb which belongs to *Lamiaceae* family (Mahmoudi, 2014). The essential oil of *Mentha longifolia* L. is obtained from various parts of the plant and has many applications in the food, pharmaceutical, and hygiene industries. Since ancient times, the leaves, flowers, and stems of this plant have been used to prepare herbal teas and dairy products (Gulluce, et al., 2007; Mahmoudi, 2014). The essential oil of *Mentha longifolia* L. has both good flavor and odor, and consequently is used as a flavoring and aroma agent in various food products. The principal components of the essential oils have been identified in previous studies, and include pulegone, carvone, limonene, 1,8-cineole, menthone and piperitenone oxide (Gulluce, *et al.,* 2007; Mahmoudi, 2014; Mkaddem, *et al.,* 2009). The essential oil has been demonstrated to show antioxidant activity, antimicrobial activity against a wide range of microorganisms, and therapeutic properties: and has hence been considered as an additive in beverages, confectionery, chewing gum, and dairy products (Dhifi, Litaiem, Jelali, Hamdi, & Mnif, 2011; Golestan, Seyedyousefi, Kaboosi, & Safari, 2016).

There are various limiting factors for the application of nutraceuticals in foods and subsequently, functional food production. These factors include a low water solubility index (Gleeson, Ryan, & Brayden, 2016; Murugesan & Orsat, 2012), and chemical and biochemical instability when temperature, pH, are varied, in addition to vulnerability to enzyme attack (L. Chen, Remondetto, & Subirade, 2006). They may also have undesirable effects on food flavors and textures, coupled with poor-bioavailability (McClements, 2015; McClements, Decker, Park, & Weiss, 2009). It is therefore necessary to design treatments to overcome these constraints to enable the use of nutraceuticals in food systems. Nanoencapsulation is one of the more successful protection methods; the bioactive compounds are entrapped within a nanoscale protective shell (Bhushani, Kurrey, & Anandharamakrishnan, 2017). Nano-capsules have a higher surface to volume ratio compared to larger encapsulating structures, thus having higher solubility, improved encapsulation efficiency, more bioavailability and a better controlled release of the entrapped components (Aditya, Espinosa, & Norton, 2017; Pereira, *et al.*, 2018; Prakash, *et al.*, 2018). The encapsulation process of bioactive compounds is carried by various methods such as dispersion and freeze drying (H. Chen & Zhong, 2015), emulsifying (Y. Chen, *et al.*, 2018), spray drying (Otálora, Carriazo, Iturriaga, Nazareno, & Osorio, 2015) and coacervation (Joaquín Gomez-Estaca, Comunian, Montero, Ferro-Furtado, & Favaro-Trindade, 2016). Damage to the payload constituents contained within the structure of the capsules can occur when conventional encapsulation methods (spray drying, freeze drying) are used and this may be accompanied by untimely and incomplete release. These limitations are not commonly observed when electrohydrodynamic (EHD) processing (i.e. electrospinning and electrospraying) is used (Alehosseini, Ghorani, Sarabi-Jamab, & Tucker, 2017; Jahangiri, *et al.*, 2014; Peltonen, Valo, Kolakovic, Laaksonen, & Hirvonen, 2010).

EHD is a recent approach for nanoencapsulation of bioactive and nutraceutical compounds which has found application in the food and pharmaceutical industries (J Gomez-Estaca, Balaguer, Gavara, & Hernandez-Munoz, 2012). The process involves pumping the feed solution through a fine nozzle or spinneret and spraying it from the spinneret using an electric field for motive power. The nanofibers or nano-capsules are collected on the nearest earthed surface. If a nanofiber is formed, the process is referred to as electrospinning, and if the process leads to nano-capsule production, it is called electrohydrodynamic atomization (EHDA) or electrospraying (Ghorani & Tucker, 2015). The process is carried out at ambient temperature (Deng, Kang, Liu, Feng, & Zhang, 2017) and results in the production of both very fast, and burst release systems (Bock, Dargaville, & Woodruff, 2014). Recently, the electrospraying technique for nano-capsule formation has been used for the stabilization of food bioactive components such as lycopene (Rocio Pérez-Masiá, Lagaron, & Lopez-Rubio, 2015), β-carotene (Gómez-Mascaraque, Perez-Masiá, González-Barrio, Periago, & López-Rubio, 2017)D-limonene (Khoshakhlagh, Koocheki, Mohebbi, & Allafchian, 2017) and green tea catechins (Bhushani, *et al.*, 2017).

The choice of an appropriate encapsulation material is a critical issue in the process. A wide range of synthetic food grade polymers and biopolymers are used in the electrospraying of bioactive and nutraceutical compounds, viable microorganisms (Librán, Castro, & Lagaron, 2017) and enzymes (Yaghoobi, Majidi, ali Faramarzi, Baharifar, & Amani, 2017). However, researchers are always looking for new materials - natural biopolymers are particularly popular, as they are highly acceptable to consumers. Balangu (*Lallemantia royleana*) is a medicinal plant grown in European and Middle East countries especially Iran, it produces quantities of a viscous gummy material when its seeds are soaked in water (Najafi, Hosaini, Mohammadi-Sani, & Koocheki, 2016; Razavi, Cui, & Ding, 2016). Balangu seed gum is a flexible polymer with a high molecular weight giving it the ability to form edible films with high thermal stability, good oxygen, and moisture permeability, water solubility and thixotropic behavior; it could, therefore, be considered as an appropriate encapsulant agent (Razavi, *et al.*, 2016; Sadeghi-Varkani, Emam-Djomeh, & Askari, 2018). However, to the best of our knowledge, the development of electrosprayed capsules for Balangu seed gum has not been yet been described.

Accordingly, in this study, we developed electrosprayed Balangu seed gum nano-capsules containing *Mentha longifolia* L. essential oil. The feasibility of nano-capsule production and the effects of varying the properties of the gum encapsulant, the active agent, the addition of surfactants and the effect of these variations on morphological characteristics were evaluated. The structural properties, loading capacity and the encapsulation efficiency of nano-capsules were also studied. In addition, the kinetics and the mechanisms of the release of essential oil from the fabricated structures in various representative model food systems; namely aqueous, alcohol based, acidic or alkali, and oily foodstuffs were modeled using first order, Kopcha, Korsmeyer-Peppas, and Peppas-Sahlin empirical equations.

2. Materials and Methods

2.1. Materials

The *Mentha longifolia* L. essential oil was kindly provided by Exir Gol Sorkh Co., Ltd. (Iran). Polyvinyl alcohol (PVA) (Mw = 77,000-79,000 Da, 98% hydrolyzed) and Hexane (HPLC grade) were purchased from Sigma-Aldrich Company (USA). Tween 20 (HLB = 16.7), ethanol and acetic acid were obtained from Merck (Germany). All chemicals were used without further purification.

2.2. Methods

2.2.1 Extraction of Balangu seed gum

The extraction of Balangu seed gum was performed based on a modification of the method described by Razavi et al. (2016). Briefly, Balangu seeds were cleaned manually to remove all impurities. The seed gum was then hydrated: the seeds being soaked in distilled water with a seed to water mass ratio of 1:30 and the suspension placed in a water bath at a constant temperature of 85°C for 150 minutes. The mixture was poured slowly and at a constant rate into the extractor (Pars Khazar, JC-700P Juicer, Iran). The extraction process was repeated twice for each batch. For the purification process, the extracted Balangu seed gum solution was mixed with ethanol at a ratio of 1 to 4. Finally, the purified Balangu gum was dried in a freeze dryer.

2.2.2. Solution preparation

To prepare the sample solutions for the electrospraying process, gum solutions (0.25 and 0.5% (w/v)) were hydrated overnight at 4°C. Tween-20 polysorbate-type nonionic surfactant (at 0.06, 0.08 and 0.1% based on gum weight) was added to the gum solutions to improve sprayability. To improve the nano-capsule production efficiency, PVA was also added at levels of 0.5 and 1% (w/v); higher levels of PVA led to nanofiber formation which was not the aim of this research. Therefore, two levels of PVA (0.5 and 1%) were used in the final emulsions. Finally, *Mentha longifolia* L. essential oil (0.015 g based on gum weight) was inserted in the emulsion systems as the oil phase, and as the bioactive and flavoring compound. To prepare the oil-in-water emulsions, the coarse emulsions were first prepared by mixing with a magnetic stirrer at 300rpm for 10 min. The coarse emulsions were then homogenized using an Ultra-Turrax homogenizer (model T-25, IKA Instruments, Germany) at a speed of 13000rpm for 3 min in an iced water bath.

2.2.3. Electrospraying process

All stages of the electrospraying process were performed under constant conditions. For this purpose, 10ml of each emulsion was drawn into a plastic syringe connected to a blunt-ended Luer Lock metal syringe needle (Gauge-21, nominal outer diameter 0.8192mm, and nominal inner diameter 0.514mm, Sigma-Aldrich). The syringe was then mounted into a triple-head syringe pump that was connected to a high voltage power supply (ES-Lab RN/X, ANSTCO, Iran). The process conditions were fixed at 1mL/h pump flow rate, 25kV spinning voltage, a needle tip-to-collector distance of 150mm, in an environment of 25±3°C and a relative humidity of 22±2%.

2.2.4. Surface tension

A tensiometer (Krüss® K100 tensiometer, Germany) was used to determine the surface tension at 20°C of each sample based on the Wilhelmy plate method. The instrument was calibrated using distilled water (71.64mN/m). The results were obtained from three replicates and the average data was reported (Zaeim, Sarabi-Jamab, Ghorani, Kadkhodaee, & Tromp, 2018).

2.2.5. Emulsion viscosity

The flow behavior parameters were determined using a Brookfield viscometer (Brookfield DVIII Ultra, Brookfield Engineering Laboratories, Stoughton, MA, USA) equipped with anSC4-27 spindle at 25°C. Flow curves were acquired at shear rates of 1–82s^{-1}. All measurements were performed in triplicate. The shear stress and shear rate data were analyzed using SlideWrite Plus Graphics Software (version 7.01, USA). The flow behavior data from the samples was approximated to a power law model (Eq. 1).

$$\sigma = k\,.\gamma^{n} \qquad \textbf{Eq. 1}$$

Where σ, *k*, γ, and n are shear stress (Pa), consistency coefficient (Pa.s^n), shear rate (s^{-1}) and flow behavior index (dimensionless), respectively.

2.2.6. Morphology of nano-capsules

The morphology of the electrosprayed Balangu seed gum nano-capsules was observed using Field emission scanning electron microscopy (FESEM), using a MIRA3, TESCAN, Czech Republic). The Balangu seed gum nano-capsules were coated with gold using a sputter coater (Q150R Rotary-Pumped Sputter Coater, Quorum Technologies Ltd., UK) for 150s at 20mA and the micrographs were observed at an accelerating potential of 15kV. One hundred nano-capsules prepared from optimal treatment were selected as a sample to determine capsule size using Image-Pro Plus software (Version 7.3).

2.2.7. Photography of electrospray jet modes

A high-speed digital camera (DFK 22BUC03, The Imaging Source Company, Germany) equipped with a zoom lens was used to determine the jet mode formed at the tip of the needle. The pictures were recorded as the electrospraying process became stable (H.-H. Kim, Kim, & Ogata, 2011).

2.2.8. Fourier-transform infrared (FTIR)

The FTIR spectra were used to analyze the interaction between Balangu seed gum, PVA and the *Mentha longifolia* L. essential oil in the nano-capsules. Electrosprayed samples were mixed with KBr and pressed into pellets. The FTIR spectra were recorded in the wave number range 4000-400 cm^{-1} using an FTIR spectrometer (Bruker Alpha FTIR, US) (Khoshakhlagh, *et al.*, 2017).

2.2.9. Thermal analysis

The thermal properties of pure PVA and Balangu seed gum, free *Mentha longifolia* L. essential oil and nano-capsules PVA/gum/essential oil were tested by Differential Scanning Calorimetry (DSC, Mettler Toledo, Switzerland). Nominal 15mg samples were placed in an aluminum pan and heated from 0 to 400°C at a 10°C/min heating rate under a nitrogen atmosphere with a flow rate of 30 mL/min (Santos, *et al.*, 2014).

2.2.10. Loading capacity and encapsulation efficiency

The encapsulation efficiency of the essential oil in Balangu nano-capsules was calculated using the method described by (Wang, et al., 2017). 5mg of the nano-capsules were first washed with

1ml of distillated water to remove the surface essential oil, and then dissolved in 1ml of 50% ethanol aqueous solution for 24h. The concentration of the essential oil was measured by recording the absorbance at 281nm using a spectrophotometer (UNICO-2100, USA). The encapsulation efficiency (EE) of the essential oil in Balangu nano-capsules was determined using the following equation (Eq. 2):

$$EE\% = (W_1 \div W_2) \times 100 \qquad \textbf{Eq. 2}$$

Where W_1 and W_2 are the weight of essential oil in a certain weight of nano-capsules and weight of the essential oil in the feed solution, respectively.

Also, the loading capacity (LC) of Balangu nano-capsules was calculated by Eq. 3 (Khoshakhlagh, *et al.*, 2017):

$$LC\% = (W_1 - W_3 / W_4) \times 100 \qquad \textbf{Eq. 3}$$

Where W_3 is the amount of free essential oil for a certain weight of nano-capsules and W_4 is the weight of nano-capsules.

2.2.11. Release kinetics of the essential oil in food models

To explain the *Mentha longifolia* L. essential oil release profile from Balangu seed gum nano-capsules, the release kinetics in food models were fitted to first-order, Kopcha, Korsmeyer-Peppas and Peppas-Sahlin empirical models. The release kinetics of the essential oil were simulated in aqueous (distilled water), acidic (3% acetic acid), alcoholic or alkali (10% ethanol) and oily (50% ethanol) food models according to the EU Commission regulation 10/2011 EU (10/2011/EC) (Atay, et al., 2018).

The first order model (Eq. 4), which is a mathematical model describes the release of the loaded compounds from porous structures (Costa & Lobo, 2001).

$$\ln M_t = \ln M_0 - K_1 \times t \qquad \textbf{Eq. 4}$$

Where M_t is the amount of essential oil released at time t, M_0 is the amount of essential oil released at time 0 and K_1 is release constant of the first order model (Desai, Singh, Simonelli, & Higuchi, 1966).

The Kopcha model (Eq. 5) is based on the release of bioactive components from a delivery system by diffusion or erosion mechanisms.

$$Mt = A \times t^{0.5} + B \times t \qquad \textbf{Eq. 5}$$

Where M_t is the amount of essential oil released at time t, A is the diffusion rate constant and B is the erosion rate constant. The A/B ratio is used to predict the dominant mechanism in the release of essential oil from the delivery system structure. If the diffusion is the dominant mechanism, the ratio of A/B would be >1 and if the release rate is governed by erosion, the ratio would be <1. If both mechanisms are involved in the release of essential oil, A/B = 1 (Kopcha, Lordi, & Tojo, 1991).

In the cases that the main mechanism of release is a combination of Fickian (diffusion) and non-Fickian transfer, the Korsmeyere-Peppas equation (Eq. 6) would be the best simple semi-empirical model for explaining the release profile (Mehrgan & Mortazavi, 2010).

$$M_t/M_\infty \times 100 = kt^n \qquad \textbf{Eq. 6}$$

Where M_t and M_∞ are the amount of essential oil released at time t and the initial mass of essential oil loaded in the nano-capsules, K is the release kinetic constant and n is the release exponent. The release mechanism is determined by the n value. For spherically shaped capsules, values $n \leq 0.43$ indicate a diffusion (Fickian) mechanism, values $0.43 < n < 0.85$

represent non-Fickian diffusion and values $n \geq 0.85$ up to 1 indicate erosion mechanism of the delivery system(Lee, *et al.*, 2006).

The Peppas–Sahlin model (Eq. 7) is used to evaluate the mechanism of Fickian and non-Fickian transfer from the structure of delivery systems.

$$M_t/M_\infty = k_1 t^m + k_2 t^{2m} \qquad \textbf{Eq. 7}$$

Where k_1 is the diffusion rate (Fickian) constant, k_2 is the erosion rate constant and m is the purely Fickian diffusion exponent for a system of any configuration which exhibits controlled release. If the ratio of $k_1/k_2>1$, the bioactive profile release is described mostly by diffusion and if $k_1/k_2<1$, the loaded component release is described mostly by erosion. Also, if the ratio of $k_1/k_2=1$, both Fickian diffusion and erosion mechanisms are involved (Peppas & Sahlin, 1989).

2.2.12. Statistical analysis

Data were analyzed using a one-way analysis of variance (ANOVA) and a Duncan's Multiple Range test for a statistical significance $P \leq 0.05$, using the IBM SPSS statistics software (version 22.0, IBM Corp., USA). All experiments were performed in duplicate, and data were presented as mean ± standard deviation (SD) values.

3. Results and discussions

3.1. Surface tension

Surface tension is one of the factors that affect the electrospraying process and the morphological characteristics of the nano-capsules produced (Deng, *et al.*, 2017). Aqueous solutions with high surface tension require some modifications to the electrospraying process or feed formulation (Okutan, Terzi, & Altay, 2014). In terms of process variables, the applied voltage can be increased to overcome increased surface tension in the feed and to eject the polymer solution towards the collector, but the level of voltage is ultimately limited due breakdown of the insulation of the device (K. Kim, Kim, & Shim, 2017). Therefore, it may be appropriate to use surfactants in the feed formulation that will reduce surface tension and hence the need for elevated voltages (Stephansen, García-Díaz, Jessen, Chronakis, & Nielsen, 2016). In this study, Tween-20 was used as an emulsifier giving the side benefit of reducing the surface tension of pure Balangu seed gum in solution.

The surface tension values of the pure Balangu seed gum and the various Oil/Water (O/W) emulsions containing *Mentha longifolia* L. essential oil, Tween-20 and various PVA concentrations are shown in Table 1. By increasing the level of Balangu seed gum to 0.5%, the surface tension of pure distilled water (71.64mN/m) dropped to 60.77mN/m. This reduction of surface tension as gum concentration is increased is probably due to the reduction of the amount of water per unit volume. Also, the addition of Tween-20 (0.06 to 0.1%) in the PVA free samples reduced the surface tension in both gum ratios:0.25% (39.36 to 38.18mN/m) and 0.5% (35.02 to 31.70mN/m). Emulsifiers, due to their amphiphilic property are rapidly absorbed to the air/solution interface and reduce the surface or interfacial tension of the solution (Rocío Pérez-Masiá, Lagaron, & López-Rubio, 2014). Increasing the PVA concentration (from 0.5 to 2%) at constant Balangu gum and Tween-20 values resulted in significantly lower surface tensions (Table.1). Okutan et al. (2014) reported that the surface tension of the polymer solution significantly decreased from 36.24 to 34.91mN/m when polymer concentration was increased from 7 to 20%.

Table 1. The surface tension of pure Balangu seed gum and various Oil/Water emulsions.

3.2. Morphology of electrosprayed nano-capsules

EHD is one of the most commonly used methods in transforming a wide range of biopolymers and synthetic polymers into nano-fiber and -capsule forms. Different morphologies can be obtained by EHD processing of polymer solutions depending on the process parameters, solution properties, and environmental conditions. In process-based changes, the spinning is influenced by the applied voltage, volume feed rate, distance from the needle to collector and needle diameter (Okutan, *et al.,* 2014; Rocío Pérez-Masiá, *et al.,* 2014). The solution property-based approaches include polymer concentration, the ratio of polymer(s) in solution, solvent type, polymeric solution viscosity, surface tension, electrical conductivity, and presence of an emulsifier. Furthermore, environmental conditions such as temperature and relative humidity influence the ability to spin (Alehosseini, *et al.,* 2017; Ghorani, Alehosseini, & Tucker, 2017; Stijnman, Bodnar, & Tromp, 2011).

Capsules are easier to handle and disperse compared to equivalent nanofibers, and so are preferred for food applications (Gómez-Mascaraque, Lagarón, & López-Rubio, 2015). Therefore, the production of Balangu nano-capsules was optimized to obtain individual capsules without the co-production of fibers.

Initially, 0.25 and 0.5% pure Balangu gum solutions were electrosprayed. The results showed that the pure gum did not have enough sprayability and no droplets were produced due to the high surface tension of the solutions (Fig. 1) (Liu, *et al.,* 2017). As can be seen in Fig. 1, with a high surface tension solution (Table 1), the jet does not form at the tip of the needle and large pendant drops fall from the spinneret. When the surface tension is very high the applied electric field is insufficiently strong to produce a spray or fiber from the solution (Alehosseini, *et al.,* 2017). Tween-20 was added at 0.06, 0.08 and 0.1% (based on gum weight) as an emulsifier to reduce the surface tension (Table 1), and initiate spraying.

As shown in Fig. 2, increasing the emulsifier level from 0.06 to 0.08% at both 0.25 and 0.5% gum concentrations (Fig. 2A, 2B, 2D, and 2E), enhanced the production of nano-capsules, but increasing the amount of emulsifier from 0.08 to 0.1% reduced the density of nano-capsules on the collector (Fig. 2C and 2F). The high surface tension of aqueous solutions prevents the formation of Taylor cone and subsequently, reduces the sprayability of the polymers (Zhao, Sun, Shao, & Xu, 2016). Also, the hydrophilic nature and poor surface activity of Balangu gum are probably the other important factors in reducing the sprayability of this gum, which justifies the use of emulsifiers. Based on these results, Tween-20 was used at a level of 0.08% for further study. To improve the rate of nano-capsules production, PVA was used at 0.5, 1 and 2% as an adjunct spinning polymer.

Fig.3A-F shows the results of the effect of variation of the gum (0.25 and 0.5%) and PVA (0.5, 1 and 2%) concentration on the morphological properties of Balangu seed gum nano-capsules. In samples containing 0.25% gum, by increasing the PVA concentration from 1 to 2%, the process made nanofibers instead of nano-capsules (Fig. 3B to 3C) this is due to the reduction in repulsive forces in the charged polymeric solution (Eatemadi *et al.,* 2016). Also, the use of 0.5% gum with various levels of PVA (0.5% to 2%) (Fig. 3D, 3E and 3F) to preferentially form nanofibers is probably due to the high viscosity of the 0.5% gum solution indicating a high level of molecular scale entanglement in the polymer chains (Koski, Yim, & Shivkumar, 2004).

Spraying or spinning gums faces two major limitations. First, most of the gums produce a high viscosity in low concentrations, and second, they provide strong shear thinning properties and as a very high shear force is applied to the polymeric solution at the tip of the needle, it may make spinning problematic (Stijnman, *et al.*, 2011) (Okutan, et al., 2014). Therefore, the critical overlap concentration and shear thinning properties are the determinant factors in a successful EHD process. From examination of the results shown in Fig. 3, the nano-capsules prepared from 0.25% Balangu seed gum emulsion, 1% PVA, 0.08% Tween-20, and *Mentha longifolia* L. essential oil were selected as the optimal treatment (Fig. 4) and subsequent experiments were performed using this formulation, to efficiently produce nano-capsules. The optimal treatment gave an average capsule size of 96.53±3.41 nm.

Fig. 1. The surface tension of pure Balangu seed gum at the tip of the needle.

Fig. 2. FESEM images of Balangu seed gum (0.25 and 0.5%) nano-capsules with different levels of Tween-20 (0.06, 0.08 and 0.1% based on gum weight): A) 0.25 gum with 0.06% Tween-20, B) 0.25 gum with 0.08% Tween-20, C) 0.25 gum with 0.1% Tween-20, D) 0.5 gum with 0.06% Tween-20, E) 0.5 gum with 0.08% Tween-20 and F) 0.5 gum with 0.1% Tween-20.

Fig. 3. FESEM images of Balangu seed gum (0.25 and 0.5%) nano-capsules with different levels of PVA (0.5, 1 and 2%): A) 0.25 gum with 0.5% PVA, B) 0.25 gum with 1% PVA, C) 0.25 gum with 2% PVA, D) 0.5 gum with 0.5% PVA, E) 0.5 gum with 1% PVA and F) 0.5 gum with 2% PVA.

Fig. 4. FESEM images of Balangu seed gum nano-capsules under the optimal conditions (0.25% Balangu seed gum, 1% PVA, 0.08% Tween-20 and the *Mentha longifolia* L. essential oil).

3.3. Viscosity

The flow behavior parameters and the curve of apparent viscosity versus shear rate of the pure gum solutions and the emulsions based on gum and gum with PVA are shown in Table 2 and Fig. 4, respectively. The analysis of the rheograms showed shear thinning (pseudoplastic) behavior for all the solutions. The power law model was the better-fitting model in than Herschel-Bulkley (R^2> 0.99) and the flow behavior index was below 0.608. Most biopolymers do show a pseudoplastic behavior. Ma, Du, Yang, & Wang (2017) have also shown that the blended film-forming solution of Tara gum and PVA exhibited a shear-thinning behavior at 0.1 to 100 1/s shear rates.

Fig. 5 shows the viscosity-shear rate changes for different solution/emulsion samples. Increasing the Balangu seed gum concentration from 0.25 to 0.5% in the samples resulted in higher viscosity values (or consistency coefficient (*k*), Table 2). Since the gums will provide a high viscosity at low concentrations, increasing the concentration of Balangu seed gum from

0.25 to 0.5% dramatically increases apparent viscosity. As a result, due to high viscosity and high surface tension in the pure gum, especially at a concentration of 0.5% pure gum, there was no possibility of electrospraying.

Also, increasing the amount of Tween-20 up to 0.08% increased the viscosity and the *k* value of the solutions, but its higher amount (0.08 to 0.1%) significantly (p<0.05) decreased the viscosity of the solutions (Table 2). Although increasing the emulsifier up to 0.08% increased the viscosity, surface tension (high surface tension is one of the limiting factors in the electro-spraying process) decreased, so the 0.08% concentration of the Tween-20 was selected as the optimum value.

Surfactants can produce hydrophobic and electrostatic interactions, and promote hydrogen bonding. Therefore, they increase the interaction between polymer chains and result in higher viscosities. However, higher concentrations of surfactants have a modulating role and may therefore reduce the viscosity of the solution (Kriegel, Kit, McClements, & Weiss, 2009).

As shown in Fig. 5, increasing the PVA level from 0.5 to 2% in O/W emulsions, improves the viscosity of the feed solutions.

Increasing the PVA concentration will result in higher interactions and entanglements between the polymer and the biopolymer chains and thus increase the viscosity (Zhou, *et al.*, 2017). It is apparent that this phenomenon offsets the negative effects of the hydrocolloid pseudoplasticity under the applied process. A change in morphology from asymmetric capsules with low density to denser and more regular capsules occurred as the PVA concentration was increased (Fig. 3 A-B). Fibers were obtained for the samples at a PVA concentration of 2% (Fig 3 C-F), while the typical pseudo-spherical capsules of the electrospraying process, with a few residual fibrils, were produced at 0.5 and 1% gum/PVA concentrations.

Table 2. Rheological parameters of pure Balangu seed gum and various O/W emulsions in the power law model.

Fig. 5. The apparent viscosity of Balangu seed gum/PVA O/W emulsions (the codes in the legend refer to the row numbers of Table 2).

3.4. Evaluation of electrospray jet modes

The mode of jet formation at the tip of the spinneret is influenced by the behavior and characteristics of the polymeric solution and the process conditions. Under constant process conditions (namely, voltage, distance and pump flow rate), only the feed properties affect the jet mode (Enayati, Chang, Bragman, Edirisinghe, & Stride, 2011). The various jet modes observed during this study are shown in Fig. 6. The best jet mode in the electrospray process is the cone-jet mode. This is the most stable form of the jet in which the polymer solution will spray well (Prajapati & Patel, 2010). The cone-jet mode was observed during the electrospraying of the emulsion prepared from 0.25% Balangu seed gum emulsion, 1%PVA and, 0.08% Tween-20 containing the *Mentha longifolia* L. essential oil. This mode is influenced by the emulsion characteristics such as viscosity and surface tension. The cone-jet mode was observed during the electrospraying of emulsions 0.25% Balangu seed gum, 0.5%PVA, 0.08% Tween-20 and the *Mentha longifolia* L. essential oil and 0.25% Balangu seed gum, 2%PVA, 0.08% Tween-20 and the essential oil, however, cone jets formed instantaneously and were unstable. During the electrospraying of these two samples, dripping (dripping and micro-dripping) and the spindle formation (single and multi-spindle) modes were also observed. This is probably due to high viscosity and also interactions between the highly charged but tiny droplets (H.-H. Kim, *et al.*, 2011) in the sample containing 2% PVA (Fig.6).

In emulsions of 0. 5% Balangu seed gum, 0.5%PVA, 0.08% Tween-20, 0.5% Balangu seed gum, 1%PVA, 0.08% Tween-20 and 0.5% Balangu seed gum, 2%PVA, 0.08% Tween-20 containing the *Mentha longifolia* L. essential oil the process proceeded to produce nanofibers (beaded fibers), multi-jet and precession modes were also observed. These modes are probably due to the increased viscosity and the reduced surface tension (leading conditions toward the production of nanofibers) (Drosou, Krokida, & Biliaderis, 2017) that were observed in the emulsions (Sections 3-1 and 3-3). In the pure Balangu seed gum solution (0.25% and 0.5%) oscillating-jet mode was observed due to the high surface tension and viscosity (Table 1-2). Additionally, in all PVA-free emulsions, intermittent precession and micro-dripping modes were observed.

Fig. 6. Images of real and simulated needles with types of jet modes are formed at the tip of the needle

3.5. FTIR analysis

The FTIR analysis was used for studying possible interactions between Balangu seed gum, PVA, essential oil and Tween-20 in the electrospray nano-capsules (Fig. 7). The spectrum of Balangu seed gum gave a very broad absorbance peak at 3406 cm^{-1} that was related to the stretching vibration of O-H groups, hydrogen bonds of Balangu gum molecules as well as the existence of water molecules connected to the gum chains. The absorption bands at 2924, 1609, 1423, 1374,1315 and 1057cm^{-1} were attributed to C-H, C-OO asymmetric stretching, C-OO symmetric stretching, C-O and C-O-C stretching, respectively (Fig. 7) (Farhadi, 2017).

The spectrum of PVA, showed the specific bands of O-H, C-H stretching vibration, C=O, C-H_2bending, C-O and C-C groups at 3388, 2939, 1739, 1441, 1377, 1265, 1093, 848 cm^{-1}, respectively (Fig. 3) (Li, Kanjwal, Lin, & Chronakis, 2013).

The FTIR spectrum of Tween-20 is shown in Fig. 7. The broad peak around 3396 cm^{-1} is defined as H-bonded O-H stretching vibration. Absorptions at 2925 and 2869 cm^{-1} indicate the C–H alkane. The peaks at 1734 and 1641 are assigned to the C=O vibration and C=C bending vibrations of the alkenes are present at 1458 and 1350 cm^{-1}(García-Benjume, Espitia-Cabrera, & Contreras-García, 2009). A very sharp peak at 1107$cm^{-1}$is attributed to the C-O stretching vibration of many esters, ether, hydroxyl groups, and also the bending vibration of C-C bonds(Khoshakhlagh, *et al.,* 2017).

Pure *Mentha longifolia* L. essential oil spectra show characteristic peaks at 2953 and 2925 (C-H stretching), 1682 (N-H bending), 1455 (CH_2 bending), 1286 (C-O-C), 1130 (C-O-C stretching) and 937 cm^{-1} (C-H bending) (Fig. 7).

The FTIR spectrum of the Balangu seed gum (0.25% w/v) nano-capsules loaded by the *Mentha longifolia* L. essential oil containing 0.5 and 1% (w/v) PVA is shown in Fig. 7. As the amount of Tween-20 and the essential oil is lower than the Balangu gum and PVA concentrations in the structure of nano-capsules, most of their small peaks were integrated or vanished entirely.

The wave number of nano-capsules containing 0.5% and 1% PVA is a little different (Fig. 7). However, the waves of the samples prepared by 1% PVA are wider and higher than capsules containing 0.5% PVA. Thus, Fig. 7shows that capsules containing 1% PVA have more hydrogen bonds, probably due to the hydrogen bonds of hydroxyl groups and other functional groups of capsule constituents. The peaks around 840-850 (C-C vibration) and 1100-1110 cm^{-1} (C-O vibration) were also strengthened in the structure of both capsules which express the successful encapsulation of the *Mentha longifolia* L. essential oil within the electrosprayed nano-capsules of Balangu gum and PVA. The overall observations indicate that there has been no adverse reaction between the constituents of the nano-capsules and the loaded essential oil, so the essential oil has been successfully trapped physically. Similarly, Khoshakhlagh et al. (2017) reported that the D-limonene encapsulation in the structure of *Alyssum homolocarpum* seed gum nano-capsules reinforces the peaks related to C-C and C-O vibration bonds.

Fig.7. FTIR spectra of 0.25% Balangu seed gum/0.5% PVA nano-capsules (0.5PVA); 0.25% Balangu seed gum/1% PVA nano-capsules (1PVA); pure Balangu seed gum (Gum); *Mentha longifolia* L. essential oil (EO); pure PVA (PVA); and pure Tween-20 (Tween-20).

3.6. Thermal analysis

The thermal properties of different samples of pure PVA and Balangu seed gum, free *Mentha longifolia* L. essential oil and nano-capsules PVA/gum/essential oil (the optimal nano-capsules) were analyzed by Differential Scanning Calorimetry (DSC). In the pure PVA thermogram, an endothermic peak in the range of 187 to 211°C with a melting transition (T_m) of 199°C can be seen (Fig. 8). The T_m represents the melting temperature in PVA. The DSC thermogram of PVA also has an endothermic peak between 298.3 to 322.5°C (centered at 310.6°C) which is related to the complete decomposition of the sample (Santos, *et al.*, 2014). The pure Balangu seed gum DSC curve shows a glass transition temperature (T_g) at 95.5±5°C and a relatively wide peak in about 291.5 to 345°C (centered at 315.6°C) which is assigned to the decomposition temperature of the pure gum (Fig. 8). The thermal properties of the free *Mentha longifolia* L. essential oil were also evaluated by DSC thermograms. The DSC curve of the essential oil showed two endothermic peaks at 29.1 and 169.4°C which are related to the evaporation temperature and the complete decomposition of the essential oil. These results confirm the heat sensitivity and volatile nature of the *Mentha longifolia* L. essential oil.

DSC thermogram of the optimal nano-capsules shows only an endothermic peak around 223.5°C. As can be seen in this curve, the evaporation peak of the essential oil has disappeared which approves the successful encapsulation of the essential oil in the complex structure. In addition, the comparison of the pure samples thermogram with the complex thermogram does not indicate any additional peak which is an indication of no interaction between Balangu seed gum/PVA/*Mentha longifolia* L. essential oil (Khoshakhlagh, *et al.*, 2017).

Fig 8. DSC thermograms for Balangu seed gum (Gum), PVA, *Mentha longifolia* L. essential oil (EO) and optimum electrosprayed nano-capsule.

3.7. Loading capacity and encapsulation efficiency

The samples that resulted in nano-capsules were further evaluated for essential oil loading capacity and encapsulation efficiency tests (Fig. 3 A-B). Table 3 shows the encapsulation efficiency and loading capacity of *Mentha longifolia* L. essential oil in the Balangu seed gum-PVA electrosprayed nano-capsules. By increasing the PVA concentration from 0.5 to 1%, the encapsulation efficiency and loading capacity of *Mentha longifolia* L. essential oil in electrosprayed Balangu seed gum-PVA nano-capsules increases from 81.54 to 87.82% and 77.56 to 84.68%, respectively.

This behavior is probably related to the higher viscosity of the emulsion containing 0.25% Balangu, 1% PVA, and *Mentha longifolia* L. essential oil than the emulsion sample containing 0.25% Balangu, 0.5% PVA, and the essential oil (Table 2 and Figure 5). The higher viscosity in the emulsion system will result in an improved stability, and will increase the loading capacity and encapsulation efficiency (Yeo & Park, 2004).

PVA and Balangu gum form hydrogen-bonded water molecules through the hydroxyl groups in their structure. This leads to the formation of a hydrated layer at the surface of the droplets and subsequently, an increase in the encapsulation efficiency and loading capacity will occur (Song, et al., 2008). Bhushani et al. (2017) investigated the efficiency of the electrospray method for encapsulation of green tea catechins. They reported that the encapsulation efficiency of zein nano-capsules ranged from 86.84 to 97.45 %. However, Khoshakhlagh et al. (2017) reported loading capacity and encapsulation efficiency were between 9.21 to 20.13% and 74.93 to 93.24%, respectively, for D-limonen in electrosprayed *Alyssum homolocarpum* seed gum nano-capsules. These differences are probably related to the emulsification method, encapsulant materials, and process conditions.

Table 3. Encapsulation efficiency and loading capacity of different electrosprayed Balangu seed gum/PVA nano-capsules

3.8. Release kinetics of the essential oil in food models

The nano-capsules prepared from 0.25% Balangu seed gum emulsion containing 1% PVA, 0.08% Tween-20, and the *Mentha longifolia* L. essential oil had the highest loading capacity and encapsulation efficiency (Table 3). So, this sample was chosen as the best candidate for examining essential oil release. The *in vitro* release kinetics of the *Mentha longifolia* L. essential oil from an optimal sample is shown in Fig. 9. The amount of essential oil released at different times was measured at 281 nm. As illustrated in Fig. 9, the *Mentha longifolia* L. essential oil release profile was a function of the type of food model. In all the model food models, the essential oil had an explosive and immediate release in the first 3 minutes. After 3 minutes, their release was continued gradually at a gentle gradient, for 60, 120, 180 and 180 minutes for distilled water, 10% ethanol, 50% ethanol and 3% acetic acid media, respectively. As the results show, the highest release from the nano-capsules was obtained in distillated water, 10% ethanol, 50% ethanol and 3% acetic acid media, respectively.

It is believed that surface erosion, disintegration, diffusion, and desorption are the mechanisms involved in the release of bioactive compounds and drug from nano-capsules and microcapsules (Hariharan, *et al.*, 2006). Therefore, to determine the mechanism of release of *Mentha longifolia* L. essential oil from Balangu seed gum nano-capsules, the release profile within various food model systems was fitted with different kinetic equations. In our study, first-order, Kopcha, Korsmeyer-Peppas and Peppas-Sahlin models were used to evaluate the release behavior of the essential oil. The constants and the coefficient of determination (R^2) of each model are shown in Table 4. Concerning the R^2 values, the first-order and the Kopcha models are not suitable for determining the release behavior of the essential oil from the nano-capsules structure. The Peppas-Sahlin model with an R^2 over 0.9945 was chosen as the appropriate model for explaining the release kinetics of the *Mentha longifolia* L. essential oil.

In the Peppas-Sahlin model, K_1 and K_2 are diffusion and erosion constants, respectively. As the ratio of K_1 to K_2 was greater than 1 so the *Mentha longifolia* L. essential oil release was mostly governed by diffusion mechanism in all food models studied (Peppas, *et al.*, 1989). However, the power of the Korsmeyer-Peppas equation (n) was lower than 0.43 (between 0.09939 and 0.1163), which indicates a Fickian mechanism of release (Lee, *et al.*, 2006).

As shown in Table 4, in the Kopcha model, the ratio of A/B is greater than 1, which indicates the predominance of the diffusion phenomenon (Fickian behavior) in the release of the *Mentha longifolia* L. essential oil in all media. Also, the comparison of diffusion (k_1) and erosion constants (k_2) in the Peppas-Sahlin model (Table 4) shows that the release mechanism of the essential oil from the structure of nano-capsules of the Balangu seed gum is mainly governed by the Fickian diffusion phenomenon since the ratio k_1/k_2 is greater than 1.

Fig. 9 shows that the highest amount of the essential oil is released in distilled water media, followed by 10% ethanol and 50% ethanol media. The lowest release rate is observed in a medium containing 3% acetic acid. Probably since Balangu seed gum and PVA are both water-soluble and have high solubility in water, so Balangu seed gum/PVA nano-capsules have a high solubility and swelling degree in distilled water, which results in the more and faster release of the essential oil in the distilled water media. However, due to the insolubility of these two polymers in alcohol and acetic acid (note that the gum is sparingly soluble in acetic acid), the swelling and solubility of the nano-capsules decrease in higher alcohol-containing and acetic acid media, swelling and solubility being ultimately lower than in distilled water media.

Table 4. Kinetics constant of the *Mentha longifolia* L. essential oil release profile in different food models

Fig.9. The cumulative release profile of the *Mentha longifolia* L. essential oil in different aqueous food stimulants.

4. Conclusion

In this study, EHDA or electrospraying process of Balangu seed gum/PVA nano-capsules loaded by *Mentha longifolia* L. essential oil was investigated. FESEM examination indicated that the emulsion containing 0.25% Balangu seed gum, 1% PVA, 0.08% Tween-20, and *Mentha longifolia* L. essential oil could be considered as the optimal formulation for nano-capsule production. FTIR spectra and DSC indicated that no undesirable interactions were occurred between Balangu seed gum/PVA and loaded *Mentha longifolia* L. essential oil. The Peppas-Sahlin model was chosen as the best model for predicting the essential oil release profile in simulated aqueous foods. Release kinetics of *Mentha longifolia* L. essential oil in simulated media followed a Fickian diffusion mechanism. The results showed a burst release of *Mentha longifolia* L. essential oil within the first 3 min, followed by sustained release for a further 180min. The results of this study showed that Balangu seed gum could be considered as a fruitful natural source for production of nano-capsules containing *Mentha Longifolia* L. essential oil. Concerning the observed release mechanism, these nano-capsules would be a good choice for fast- flavor release systems (the system is under study and development by the authors).

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Highlights:

- Electrospray-assisted fabrication of Balangu seed gum nano-capsules was optimized;
- The effects of processing parameters on morphology and properties were studied;
- *Mentha longifolia L.* essential oil was electro-encapsulated in the nano-capsules;
- The types of jet-modes were reported for electrospraying of Balangu seed gum;
- Kinetic modeling ws applied to essential oil release from Balangu nano-capsules;
- Different release behaviors of *Mentha longifolia L.* essential oil were studied.